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# PATENT SPECIFICATION

NO DRAWINGS

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Inventors: HERBERT AUBREY STEVENSON, JOHN RAY MARSHALL and ANTHONY FREDERICK HAMS.

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International Classification:—C07c (A01n).

## COMPLETE SPECIFICATION

### New Fungicidal Compositions and Compounds

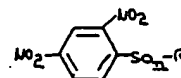
We, BOOTS PURE DRUG COMPANY LIMITED, a British Company, of Station Street, Nottingham, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fungicidal compositions and to methods for the control of fungi. In this specification the term "fungicidal" is not to be given its strictly scientific meaning but is intended to mean "capable of controlling the growth of fungi."

Plant pathogenic fungi can in many instances cause considerable loss of agricultural and horticultural crops and many compounds are in current use for controlling such fungi in order to diminish this loss. However the compounds presently available are by no means completely adequate, owing to the great variation of crops and fungi pathogenic thereto, and the search for more effective fungicides continues. In spite of the considerable amount of research and experimentation towards this end, it is not possible to forecast the value of untested compounds as agricultural and horticultural fungicides. The fact that the fungicides must not deleteriously affect the crops adds considerably to the difficulty of obtaining satisfactory products.

It is an object of the present invention to provide novel fungicidal compositions and methods of controlling the growth of fungi pathogenic to agricultural and horticultural crops. It is a further important object of the invention to provide novel fungicidal compositions which combine high, wide spectrum fungicidal activity with low phytotoxicity, and low mammalian toxicity.

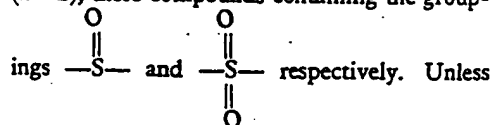
According to one feature of the present invention there are provided fungicidal compositions which comprise a compound of the general formula I



..... I

wherein  $n$  represents 1 or 2 and (a) when  $n=1$ , R represents a radical selected from alkyl containing 5—7 carbon atoms, cycloalkyl, phenylalkyl, phenylalkyl in which the phenyl nucleus contains one or more substituents selected from halogen atoms and nitro groups, phenyl and phenyl which contains one or more substituents selected from halogen atoms, nitro, alkyl, alkoxy and alkoxy-carbonyl groups; (b) when  $n=2$ , R represents a radical selected from alkyl, halogenated methyl, halogenated propyl, cycloalkyl, phenylalkyl and phenylalkyl in which the phenyl nucleus contains one or more substituents selected from halogen atoms and nitro groups; in association with an inert fungicidal adjuvant.

The compounds of the above general formula I are either sulphoxides ( $n=1$ ) or sulphones ( $n=2$ ), these compounds containing the group—



otherwise defined, the terms "alkyl" and "cycloalkyl" used in the definition of compounds of general formula I are intended to mean such radicals containing up to seven carbon atoms.

We have found that compounds of general formula I possess high fungicidal activity against a wide range of fungi which are pathogenic to horticultural and agricultural crops, and that these compounds are virtually non-phytotoxic to a wide variety of crops. Thus, for example, they are fungicidal against

*Venturia* spp., *Phytophthora* spp., genera of the family *Peronosporaceae*, *Cladosporium* spp., *Alternaria* spp., *Septoria* spp., *Botrytis* spp., *Sclerotinia* spp. and *Gloeosporium* spp., and substantially non-phytotoxic towards apples, pears, tomatoes, potatoes, vines, celery, broad beans, french beans, and roses. Accordingly they are of value for the treatment of such diseases as apple scab (*Venturia inaequalis*), pear scab (*Venturia pirina*), potato blight (*Phytophthora infestans*), downy mildew (*Plasmopora viticola*) on vines, and early blight (*Alternaria solani*) of potatoes, celery leaf spot (*Septoria api*), chocolate spot (*Botrytis fabae*) on broad beans, brown rot (*Sclerotinia fructicola*) of stone fruits, tomato leaf mould (*Cladosporium fulvum*) and bitter rot of apples and fruit tree canker (*Gloeosporium perennans*). This list is given by way of example only and is not intended to limit the invention.

The term "inert fungicidal adjuvant" used in this specification is to be interpreted as meaning any diluent or carrier which may be used for the formulation of fungicidal compounds for the treatment of horticultural and agricultural crops or the ground in which the crops are growing or are to be grown. Typical adjuvants include dispersing agents, emulsifying agents, wetting agents, pulverulent solid dusting powders, volatile propellants and ignitable slow-burning compositions.

The compositions of the invention may take a variety of forms and include dusting powders, dispersions, emulsions, smokes and aerosols. In particular the dispersions and emulsions may be supplied to the consumer as such and at the required concentration of active material or they may be supplied as primary compositions which require the addition of water either to dilute them to the desired concentration of active ingredient or actually to form the dispersion or emulsion. The invention includes both the primary and the final compositions.

The concentration of the active material in the primary compositions which may be provided for the preparation of any of the forms in which the compositions of the present invention may be used may vary widely. For example the amount of active material present in a finely ground dispersible powder may be limited to less than 50% if the active material has a relatively low melting point and tends to melt in the grinding and mixing process. On the other hand if it has a relatively high melting point a dispersible powder containing up to 90% or more of the active material may be prepared satisfactorily. Restrictions depending on the physical properties of the active ingredient also apply in the case of e.g. solutions and emulsions, etc. When preparing the primary compositions the practicability of making highly concentrated mixtures, i.e. mixtures containing up to 90% or more of the active material must be considered for it is

obviously desirable to supply the consumer with a mixture having as high a concentration as is possible. It would be uneconomical to apply the primary compositions in their concentrated forms and it is preferred to apply mixtures containing less than 20% of the active material. For very light applications mixtures containing 0.001% of the active ingredient may be used but generally the preferred compositions for application in the field contain from 0.05 to 10% of the active ingredient.

When compositions of the present invention are provided as dusting powders they comprise one or more of the active compounds having the foregoing general formula I intimately mixed with a pulverulent solid diluent, the mixture containing up to 90% w/w of the active component.

As dispersions, the compositions of the present invention comprise essentially one or more of the active compounds having the foregoing general formula dispersed in an aqueous medium. It is convenient to supply the consumer with a primary composition which may be diluted with water to form a dispersion having the desired concentration; the primary composition may be in any one of the following forms.

It may be provided as a dispersible powder comprising the active ingredient and a suspending or dispersing agent which powder forms a dispersion when mixed with water.

In another form the primary composition may be supplied as a solution of the active ingredient in a water-miscible solvent, e.g. acetone with a dispersing agent which solution forms a dispersion when diluted with water.

A further primary composition comprises an active compound having the foregoing general formula in the form of a finely ground powder in association with a dispersing agent and intimately mixed with water to give a paste or cream which forms a dispersion when diluted with water.

The above-mentioned cream or paste comprising a finely ground active ingredient may be added to an emulsion of oil in water to give yet another type of primary composition which is a dispersion of the active compound in an aqueous oil emulsion, which may be further diluted with water before use.

The compositions of the present invention which are provided as emulsions consist essentially of one or more of the active compounds having the foregoing general formula dissolved in a solvent which is formed into an emulsion in the presence of an emulsifying agent with water. An emulsion of the desired concentration may be formed from a primary composition and the primary composition may be in one of the following forms.

It may be supplied as a concentrated stock emulsion which comprises an active ingredient having the foregoing general formula in combination with an emulsifying agent, water and

an organic solvent for example xylene or another aromatic solvent boiling within the range 80—300° C.

Another primary composition suitable for preparing emulsions may consist of the active ingredient in an organic solvent and mixed with an emulsifying agent so that an emulsion is formed when the primary composition is diluted with water.

The aerosol compositions of the present invention include (1) a solution of an active ingredient in a volatile solvent such as acetone, together with, if desired, a small amount of a non-volatile oil such as a vegetable oil and (2) a solution of an active ingredient in a high boiling aromatic solvent; if the solubility of the active ingredient in this solvent is low, it may be necessary to add a supplementary solvent such as cyclohexanone or acetone. Such compositions are readily dispersed as aerosols either by mechanical means or by incorporating therein a volatile propellant such as Freon—Registered Trade Mark—(a mixture of chloro-fluoro derivatives of methane and ethane).

Compositions suitable for the generation of fungicidal smokes comprise a compound of the foregoing general formula I in association with an ignitable slow-burning composition so that a smoke containing the active ingredient is generated when the composition is ignited. Thus such compositions may contain a fuel, for example sucrose, a source of oxygen, for example potassium chlorate, and a dampener, for example kaolin, to control the rate of burning.

In addition to the ingredients already mentioned the compositions of the invention may also contain other substances conventionally used in the art, the function of which may be to improve the handleability of the compositions or to improve their utility. For example an inert diluent such as kaolin may be used in the formulation for the preparation of a dispersible powder in order to facilitate mixing of the components and to provide sufficient bulk for mixing with water. As a further example the compositions intended for dilution with water prior to application may also contain a wetting agent in order to ensure satisfactory coverage of the leaves of the plants or trees to be treated. Also when dusts are prepared a lubricant such as magnesium stearate may be added to the mixture to promote both easier mixing of the components and to ensure that the final product has free flowing properties. Conventional "stickers", such as polyvinyl alcohol, colloid-like materials e.g. silicic acid, bentonite or casein, may also be included in the compositions of the invention to improve the persistence of the fungicide after application.

The compositions hereinbefore described wherein the active ingredients are present in solid form, e.g. dusting powders and dispersible

ingredients in the form of very fine particles; the majority of the particles, of the order of at least 95%, should be less than 50 $\mu$ , with about 75% of them being 5—20 $\mu$ . The adjuvants conventionally used in such compositions are generally of this particle size, or smaller. The compositions can be prepared by means of conventional grinding equipment such as a hammer mill.

Other insecticides and fungicides such as D.D.T., benzene hexachloride, dinocap, dinoseb dimethacrylate, and sulphur may be incorporated in the compositions of the invention before application to the plants.

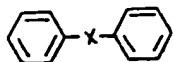
According to a further feature of the invention there is provided a process for controlling the growth of fungi on a crop which comprises treating a material selected from the crop and the soil in which the crop is to grow with a fungicidally effective amount of a compound of the foregoing general formula I. In this specification the term "crops" includes agricultural and horticultural plants either in their dormant or growing phases.

The method of using the compositions of the invention is dependent on many variables such as the particular fungus to be controlled, the severity of infection, the crop species to be treated and its environment and the size of the plants or trees, such variables influencing the application rate. Variation of method of application and application rate is well-known in the art of fungal control by chemical means and it is further known that absolutely rigid rates to suit all circumstances are impossible to define. However in general, application of the compositions of the invention at rates equivalent to about 0.2—100 lb. of active ingredient per acre gives satisfactory results. For application to foliage, rates of 0.2—8 lb. active ingredient per acre as a spray will normally be sufficient. For the control of many foliage fungi, such as for example *Venturia inaequalis*, rates of 0.5—2 lb. active ingredient per acre as a spray are frequently sufficient. Dusting powder application rates will normally be higher, within the aforesaid 0.2—100 lb./acre range.

The compounds of general formula I which we have found to possess outstanding value as fungicides for use in horticulture and agriculture all contain a 2,4-dinitrophenyl nucleus, attached either to a sulfoxide group or to a sulphone group. These characteristics would appear to be necessary for high fungicidal activity as will be seen on comparing the results of experiments described hereafter using compounds of general formula I and a representative selection of closely related compounds falling outside the scope of the invention. The nature of the radical R, which is attached to the sulfoxide or sulphone group, additionally influences the value of the compounds as plant fungicides; outside the definitions of R in

general formula I as previously described, diminished fungicidal activity and/or increased crop phytotoxicity becomes evident, as will be seen from a study of experimental results hereinafter described.

- 5 It is known from Swiss Patent Specification No. 262,191 that diphenyl compounds of the general formula II



..... II

- 10 in which X represents sulphur or a sulphur containing group, e.g. SO, SO<sub>2</sub>, or SS, and in which the phenyl groups may bear substituents for example halogen atoms, copper, mercury, sulpho, nitro, nitroso or ether groups, are  
15 fungicides. It is further stated in this Swiss patent specification that especially active fungicides are obtained by substitution at the 4- and 4,4'-positions. However the extremely high, wide spectrum activity and substantial  
20 non-phytotoxicity of the compounds of the aforementioned general formula I, which are the active ingredients of the compositions of the present invention, could not have been predicted from Swiss patent specification No.  
25 262,191. Although this patent specification includes within its very broad definition of active agents some of the compounds of general formula I, there is no specific disclosure of this latter type of compound and the specification gives no indication that such a group  
30 of narrowly defined compounds would be markedly superior to closely related compounds such as those that are specifically mentioned in the Swiss specification.

- 35 It is also known from Summary Tables of Biological Tests, February 1954, page 10 that beta-chloroethyl 2,4-dinitrophenyl sulphoxide is active at 10 p.p.m. in a spore germination test against *Stemphylium*  
40 *sarcinaeforme* and *Sclerotinia fructicola*. No details are given of the effect of this compound on living plants. In fact examination of this substance has revealed that it is too phytotoxic to plants for it to have any practical  
45 value as a fungicide in agriculture and horticulture.

- The following list of compounds, which is given by way of example only and is not to be interpreted as limiting the invention in any  
50 way, is representative of the compounds of the foregoing general formula I which may constitute active ingredients of the invention.

#### 2,4-Dinitrophenyl X sulphoxide.

- 55 X = n-pentyl, m.p. 66—69° C.  
n-hexyl, m.p. 63—65° C.  
n-heptyl, m.p. 74—76° C.  
3-methylbutyl, m.p. 67—68° C.

cyclopentyl, m.p. 119° C.	
cyclohexyl, m.p. 140° C.	60
benzyl	
p-chlorobenzyl, m.p. 152—153° C.	
p-nitrobenzyl, m.p. 184—186° C.	
phenyl	
p-chlorophenyl, m.p. 144—145° C.	
p-bromophenyl, m.p. 138—140° C.	65
p-fluorophenyl, m.p. 117—118° C.	
p-tolyl, m.p. 131—134° C.	
p-nitrophenyl, m.p. 163—164° C.	
m-nitrophenyl, m.p. 210—212° C.	70
4-bromo-3-nitrophenyl, m.p. 180—182° C.	
4-chloro-3-nitrophenyl, m.p. 182—185° C.	
2-chloro-4-methylphenyl, m.p. 145—148° C.	
2-chloro-5-methylphenyl, m.p. 210—212° C.	75
2,5-dichlorophenyl, m.p. 216—220° C.	
2,5-dichloro-x-nitrophenyl, m.p. 238—242° C.	
p-methoxyphenyl, m.p. 150—152° C.	
o-methoxycarbonylphenyl	80
p-methoxycarbonylphenyl, m.p. 133—135° C.	
p-methoxycarbonyl-x-nitrophenyl, m.p. 240—242° C.	
2,4-Dinitrophenyl Y sulphone.	85
Y = methyl	
ethyl	
n-propyl	
iso-propyl	
n-butyl	90
iso-butyl	
sec-butyl	
n-pentyl	
3-methylbutyl, m.p. 121—122° C.	
1-methylbutyl, m.p. 117—118° C.	95
n-hexyl	
n-heptyl	
cyclopentyl, m.p. 180—181° C.	
cyclohexyl	
dichloromethyl, m.p. 150—152° C.	100
dibromomethyl, m.p. 158—160° C.	
3-chloropropyl, m.p. 80—81° C.	
benzyl	
p-nitrobenzyl, m.p. 229—232° C.	105
p-chlorobenzyl, m.p. 184—185° C.	

Many of the compounds falling within general formula I have not previously been described; in the above list melting points of such compounds are given. The new compounds are prepared by methods similar to those known for the old compounds.

The listing of the above compounds is not meant to indicate that they are all of equal value for the control of fungi on agricultural and horticultural crops. The control of such fungi is desirable from both the protectant point of view and the eradicator point of view. That is to say it is desirable that a fungicide be capable of controlling the growth of fungi

when applied to the crop either a few days before or a few days after infection takes place, as well as when application and infection take place on the same day.

5 The compounds of general formula I have been studied against several fungi and the preferred compounds in so far as degree of fungicidal activity is concerned include (a) the  
10 sulphones (i.e.  $n=2$ ) in which R is an alkyl, halogenated methyl or halogenated propyl radical, alkyl containing 3—6 carbon atoms being most preferred, and (b) the sulphoxides  
15 (i.e.  $n=1$ ) in which R is a phenyl or substituted phenyl radical. As a result of considerable investigation into comparative degrees of activity, spectrum of activity, and protectant and eradicant abilities, the most preferred compounds include the sulphones wherein R is *n*-butyl, *n*-pentyl and iso-butyl and the sulphoxides wherein R is *p*-methoxycarbonyl-phenyl and *p*-tolyl. These five compounds are  
20 not necessarily of equal value.

The compounds of general formula I have been shown to have high fungicidal activity in tests carried out in the following manner:—

25 On a glass slide a deposit of known weight of the compound under test is formed by allowing 0.25 ml. of an acetone solution of known concentration of the compound to evaporate.  
30 Spores of *Venturi inaequalis* in aqueous suspension are set on these deposits (0.05 ml. of a 50,000 spores/ml. suspension) to germinate and after 18 hours incubation the percentage germination is noted. In the following tables  
35 the results of these tests are shown, the

"approximate L.D. 50" being the concentration in parts per million of the acetone solution of the substance under test which it is estimated would inhibit 50% of the spores from germinating; the higher the value of the L.D. 50, the lower the activity of the compound. It should be noted that when a result is quoted as <2, <4 etc., this means that this concentration is the least used in the test and that on further testing a figure of <1 or <0.5  
40 45 may be obtained.

This test measures the ability of a compound to control the fungus. Without this ability at low concentration, a compound is not likely to be of outstanding value for the control of fungi on plants. However, as later results will indicate, this type of test merely separates the compounds of no value from the compounds of possible value. It cannot be said that all compounds showing a very small L.D. 50 in this test are definitely valuable for the control of fungi on plants. Stability on the leaf, persistence, inactivation by the plant, phytotoxicity and many other factors must be considered and two compounds with identical L.D. 50's of a low order may behave quite differently on plants. The compounds of general formula I have been examined in this way, as later results indicate. 50 55 60

Table I: In this table are shown the results obtained using a representative selection of compounds falling within general formula I, and which may be used according to the present invention: 65

TABLE I

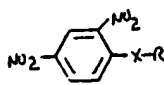
			
X	R	Type of R	Approximate L.D. 50
SO	n-pentyl n-hexyl n-heptyl 3-methylbutyl	C <sub>3-7</sub> alkyl	<2 <2 <2 3
SO	cyclopentyl cyclohexyl	cycloalkyl	3 6
SO SO SO	benzyl p-chlorobenzyl p-nitrobenzyl	phenylalkyl	<2 3 <2
SO SO SO SO SO SO SO SO SO SO SO SO SO SO SO SO SO SO	phenyl p-chlorophenyl p-bromophenyl p-fluorophenyl p-tolyl p-nitrophenyl m-nitrophenyl 4-bromo-3-nitrophenyl 4-chloro-3-nitrophenyl 2-chloro-4-methylphenyl 2-chloro-5-methylphenyl 2,5-dichloro-x-nitrophenyl 2,5-dichlorophenyl 2,4-dinitrophenyl p-methoxyphenyl o-methoxycarbonylphenyl p-methoxycarbonylphenyl p-methoxycarbonyl-x-nitrophenyl	phenyl	3 <2 <2 <2 <2 <2 3 <2 <2 2 <2 <2 <2 6 <2 3 <2 <2 3 6 6 6 6
SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub>	methyl ethyl n-propyl iso-propyl n-butyl iso-butyl sec-butyl n-pentyl 3-methylbutyl 1-methylbutyl n-hexyl n-heptyl	alkyl	<2 <2 <2 <2 3 <2 <2 <2 4 6 6 6 6
SO <sub>2</sub> SO <sub>2</sub>	cyclopentyl cyclohexyl	cycloalkyl	<2 2
SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub>	dichloromethyl dibromomethyl 3-chloropropyl	haloalkyl	<2 <2 2
SO <sub>2</sub> SO <sub>2</sub>	benzyl p-nitrobenzyl	phenylalkyl	6 7



Table II: In this table are shown the results obtained using several compounds closely related to but distinct from the compounds of general formula I. These compounds are all sulfoxides or sulphones attached to a radical W which falls within the definition of R in general formula I, but they do not contain the 2,4-dinitrophenyl radical which is an essential feature

of the compounds of the invention. The compounds listed are a representative selection of the large number of compounds of this type which have been examined. Those marked \* are either specifically mentioned in or covered by the general formula of Swiss patent No. 262,191 which has been discussed hereinbefore.

TABLE II

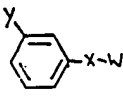
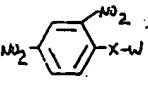
				
Y	X	W	Type of W	Approximate LD 50
p-NO <sub>2</sub>	SO	benzyl	phenylalkyl	> 300
p-NO <sub>2</sub>	SO <sub>2</sub>	benzyl		> 300
o-NO <sub>2</sub>	SO	benzyl		> 300
o-NO <sub>2</sub>	SO <sub>2</sub>	benzyl		> 300
p-NO <sub>2</sub>	SO	p-chlorobenzyl		> 300
p-NO <sub>2</sub>	SO <sub>2</sub>	p-chlorobenzyl		> 300
H	SO	*phenyl	phenyl	50
p-NO <sub>2</sub>	SO	*p-nitrophenyl		> 300
p-NO <sub>2</sub>	SO	*p-chlorophenyl		> 300
p-NO <sub>2</sub>	SO	*p-tolyl		> 300
o-NO <sub>2</sub>	SO	p-chlorophenyl		70
2,4,6-(NO <sub>2</sub> ) <sub>3</sub>	SO	*p-tolyl		50
4-Cl-2,6-(NO <sub>2</sub> ) <sub>2</sub>	SO	*phenyl		70
m-NO <sub>2</sub>	SO <sub>2</sub>	methyl	alkyl	60
m-NO <sub>2</sub>	SO <sub>2</sub>	n-pentyl		> 300
p-NO <sub>2</sub>	SO <sub>2</sub>	t-butyl		> 300
p-NO <sub>2</sub>	SO <sub>2</sub>	1-methylbutyl		> 300
4-CH <sub>3</sub> -3-NO <sub>2</sub>	SO <sub>2</sub>	n-propyl		> 300
4-CH <sub>3</sub> -3-NO <sub>2</sub>	SO <sub>2</sub>	iso-butyl		> 300
4-CH <sub>3</sub> -3-NO <sub>2</sub>	SO <sub>2</sub>	3-methylbutyl		> 300
4-Cl-3-NO <sub>2</sub>	SO <sub>2</sub>	ethyl		50
4-Cl-3-NO <sub>2</sub>	SO <sub>2</sub>	n-propyl		> 300
4-Cl-3-NO <sub>2</sub>	SO <sub>2</sub>	n-butyl		> 300
4-Cl-3-NO <sub>2</sub>	SO <sub>2</sub>	3-methylbutyl		> 300
4-Cl-3-NO <sub>2</sub>	SO <sub>2</sub>	n-pentyl		70
p-NO <sub>2</sub>	SO <sub>2</sub>	dibromomethyl	haloalkyl	50
p-NO <sub>2</sub>	SO <sub>2</sub>	dichloromethyl		> 80
p-NO <sub>2</sub>	SO <sub>2</sub>	3-chloropropyl		> 300
p-NO <sub>2</sub>	SO <sub>2</sub>	1-chloroethyl		> 300

Table III: More compounds are included which are closely related to but distinct from the compounds of general formula I. In this case, the compounds possess the characteristics of the compounds of the invention in so far as the 2,4-dinitro and W radicals are concerned, but in place of the sulfoxide or sulphone groups, there

is a sulphide or disulphide group. The compounds listed are a representative selection of the large number of compounds of this type which have been examined. Those marked \* are either specifically mentioned in or covered by the general formula of Swiss patent No. 262,191.

TABLE III

			
X	W	Type of W	Approximate LD 50
S	benzyl	phenylalkyl	> 400
S	p-chlorobenzyl		> 400
S	p-nitrobenzyl		> 400
S	*p-chlorophenyl	phenyl	> 400
S	*p-nitrophenyl		80
S	*p-tolyl		> 400
S	*2,5-dichlorophenyl		80
S	*2,4-dinitrophenyl		80
S	*o-methoxycarbonyl		80
S	*p-methoxycarbonyl		> 80
S—S	*p-tolyl		> 80
S—S	*2,4,6-trichlorophenyl		> 80
S	methyl	alkyl	> 80
S	n-propyl		> 80
S	n-butyl		> 80
S	sec-butyl		> 80
S	n-pentyl		> 80
S	n-hexyl		> 80
S—S	n-pentyl		50
S	beta-chloroethyl	haloalkyl	20
S	beta-bromoethyl		80
S	cyclohexyl	cycloalkyl	> 80

As stated before, the compounds of general formula I are substantially non-phytotoxic to a wide variety of agricultural and horticultural plants. Thus the compounds previously listed in Table I have been found to be suitable for application to plants in conventional spraying programme routines. The difficulty of finding high fungicidal activity and low phytotoxicity in a compound is illustrated by

the results shown in Table IV. Some of the compounds therein listed showed high fungicidal activity in the spore germination test hereinbefore described, but on being applied to plants they caused sufficient damage to render their use to control fungi on plants impossible. The close similarity of these compounds to those falling within the invention is to be noted.

TABLE IV

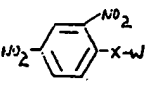
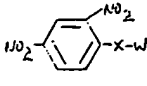
			
X	W	Approximate LD 50	Effect on Tomatoes
SO	methyl	< 4	damage
SO	ethyl	< 2	damage
SO	n-propyl	< 2	damage
SO	n-butyl	> 80	damage
SO	iso-butyl	< 2	damage
SO	beta-chloroethyl	6	damage
SO <sub>2</sub>	beta-chloroethyl	10	damage

Table V: The compounds herein listed, although possessing the 2,4-dinitrophenyl nucleus and either the sulfoxide or sulphone group do not fall within general

formula I; these results are shown to illustrate further the unpredictability of the properties of the compounds of the invention.

TABLE V

		
X	W	Approximate LD 50
SO <sub>2</sub>	p-tolyl	> 400
SO <sub>2</sub>	p-carboxyphenyl	80
SO	o-carboxyphenyl	80
SO	p-carboxyphenyl	80
SO <sub>2</sub>	n-octyl	50
SO <sub>2</sub>	n-decyl	> 80
SO <sub>2</sub>	n-dodecyl	> 80
SO <sub>2</sub>	3,5,5-trimethylhexyl	> 80
SO <sub>2</sub>	beta-phenoxyethyl	50

The compounds of general formula I have been subjected to intensive study to ascertain their value for the control of fungi on growing crops. Thus, for example, a series of trials have been carried out in the greenhouse as follows:

Groups of young plants were sprayed with an aqueous dispersion of the compounds under test, six plants per treatment and 100 ml. of spray for the six plants. The concentration of active agent in the spray was usually 0.05% or less, equivalent to 1 lb. active ingredient per acre. The plants were inoculated with the

fungus under study by spraying them with an aqueous spore suspension and were then maintained in a humidity chamber for 48 hours to allow the spores to germinate, if allowed to by the chemical. They were then kept in the greenhouse for 7—21 days, depending on the fungus and at the end of this time an assessment of the fungicidal effect of each treatment was carried out by a careful quantitative examination of the area of leaf damage and comparison of treated plants with untreated control plants. Three types of such test were:

celery and *Botrytis fabae* on broad beans. Some typical results are shown in Table VI. (Figures indicate % control).

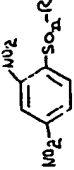
(c) Eradicant: Spraying took place some time after inoculation. Thus E+2 means that spraying took place two days after inoculation.

Fungi and crop plants used included *Venturia inaequalis* on apples, *Cladosporium fulvum* on tomatoes, *Phytophthora infestans* on tomatoes, *Plasmopora viticola* on vines, *Septoria apii* on

(a) Routine: the plants were inoculated with the fungal spores as soon as dry after spraying with the chemical.

(b) Protectant: Spraying took place some time before inoculation. Thus P-2 indicates that inoculation took place two days after spraying, P-3 three days after, and so on.

TABLE VI

Fungus	V.I.		P.I.	C.F.		P.V.		S.A.		B.F.	
	Routine	P-3		P-4	E+4	P-3	E+1	Routine	P-4	P-3	P-1
Concentration %	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
											
R											
n-penyl	100	93	100	63.3	32.5	99.4	83.4	99.7	91.5	73.5	92.8
iso-butyl	2	99	100	86	25.5	94.3	74.5	98.7	94.4	87.2	95.3
p-tolyl	1	80	100	65.6	28.1	92.8	52.2	99.6	73.5	83.9	97.3
p-methoxy-carbonylphenyl	1	97	100	55	49.2	100	84.6	97.8	94.4	85.4	86.2
Captan <sup>(1)</sup>	100	99	—	—	27.5	76.7	—	—	—	—	—
Zineb <sup>(2)</sup>	—	—	100	60	—	—	72.7	—	—	—	—
Copper oxychloride <sup>(3)</sup>	—	—	—	—	—	—	—	89.4	73.8	—	—

<sup>(1)</sup> Used at the standard rate of 1 lb. active ingredient/100 gal.

<sup>(2)</sup> Used at the standard rate of 1.4 lb. active ingredient/100 gal.

<sup>(3)</sup> Used at the standard rate equivalent to 0.38 lb. copper/100 gal.

V.I. = *Venturia inaequalis*

P.I. = *Phytophthora infestans*

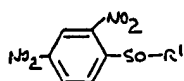
C.F. = *Cladosporium fulvum*

P.V. = *Plasmopora viticola*

S.A. = *Septoria apii*

B.F. = *Botrytis fabae*

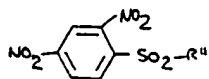
According to a further feature of the invention there are provided new chemical compounds of the general formula III



..... III

- 5 wherein R<sup>1</sup> represents an alkyl radical containing 5—7 carbon atoms, a halogenated and/or nitrated benzyl radical, a cycloalkyl radical, or a substituted phenyl radical in which the substituents are chosen from halogen atoms, nitro, alkyl, alkoxy and alkoxy carbonyl radicals, provided that R<sup>1</sup> does not represent 2,4 - dinitrophenyl or *o* - methoxycarbonyl-phenyl.

- 15 According to a further feature of the invention there are provided new compounds of the general formula IV

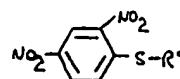


..... IV

- 20 wherein R<sup>11</sup> represents a dichloromethyl, dibromomethyl, 3-chloropropyl or a halogenated and/or nitrated benzyl radical.

- 25 The new compounds of the invention may be conveniently prepared by oxidation of the corresponding sulphides. The particular method chosen for carrying out this oxidation is dependent on the nature of the radical represented by R<sup>1</sup> or R<sup>11</sup>; suitable methods include oxidation by means of hydrogen peroxide (or

a suitable per-acid) or nitric acid. Alternatively some of the new compounds of the invention may be prepared by oxidising a sulphide of the general formula V



..... V

in which R<sup>2</sup> is a radical readily transformable into the desired radical R<sup>1</sup> or R<sup>11</sup> by subsequent treatment, and treating the sulfoxide or sulphone so obtained by suitable means to produce a radical R<sup>1</sup> or R<sup>11</sup> in place of R<sup>2</sup>.

The following non-limitative examples illustrate the invention.

#### EXAMPLE 1.

In the preparation of a dusting powder, 5 parts by weight of isobutyl 2,4-dinitrophenyl sulphone were intimately mixed with 95 parts by weight of kaolin and the mixture subjected to hammer-milling.

#### EXAMPLE 2.

In the preparation of a dispersible powder, 20 parts by weight of *p*-chlorophenyl 2,4-dinitrophenyl sulfoxide were intimately mixed with 8 parts by weight of Belloid T.D. (a proprietary dispersing agent—a condensate of formaldehyde and an alkylaryl sulphonate) and 72 parts by weight of kaolin, and the mixture hammer-milled. This composition forms an aqueous dispersion of active ingredient on dilution with water.

#### EXAMPLE 3.

Dispersible powders were prepared by hammer-milling the following mixtures (parts by weight).

(a) Isobutyl 2,4-dinitrophenyl sulphone	50%
Belloid T.D. (Registered Trade Mark)	3%
Nansa S (a proprietary wetting agent, the sodium salt of an alkylaryl sulphonic acid)	2%
Kaolin	to 100
(b) Isobutyl 2,4-dinitrophenyl sulphone	50%
Belloid T.D.	2%
Ethylan C.P. (a proprietary wetting agent, a polycethylene oxide condensate of octylphenol)	0.5%
Kaolin	to 100%.
(c) Isobutyl 2,4-dinitrophenyl sulphone	50%
Tween 60 (a proprietary dispersing agent, a polyoxyethylene derivative of sorbitan monostearate)	2%
Ethylan C.P.	0.5%
Kaolin	to 100 %

(d) Is butyl 2,4-dinitrophenyl sulphone	50%
Tween 60	2.5%
Kaolin	to 100%
(e) Isobutyl 2,4-dinitrophenyl sulphone	50%
Tween 60	2%
Ethylan C.P.	0.5%
Natrosol 250 a hydroxyethylcellulose)	2%
Ground silica	to 100%
(f) Isobutyl 2,4-dinitrophenyl sulphone	50%
Tween 60	2%
Ethylan C.P.	0.5%
Colloidal silicic acid	10%
Kaolin	to 100%
(g) Isobutyl 2,4-dinitrophenyl sulphone	50%
Belloid T.D.	3%
Nansa S	2%
Bentonite	10%
Kaolin	to 100%
(h) n-Pentyl 2,4-dinitrophenyl sulphone	25%
Belloid T.D.	8%
Nansa S	2.5%
Kaolin	to 100%
(i) Isobutyl 2,4-dinitrophenyl sulphone	50%
Tween 60	1%
Nansa S	1%
Kaolin	to 100%
(j) Isobutyl 2,4-dinitrophenyl sulphone	50%
Ethylan C.P.	1%
Kaolin	to 100%
(k) 2,4-Dinitrophenyl <i>p</i> -tolyl sulfoxide	50%
Ethylan C.P.	1%
Polyviol M13/140 (a proprietary polyvinyl alcohol)	1%
Kaolin	to 100%

Compositions similar to those described in Examples 1—3 were prepared using as active ingredient other compounds hereinbefore listed.

## EXAMPLE 4.

In the preparation of a composition suitable for dilution with water to produce a stable emulsion, the following ingredients were mixed.

(a) n-Pentyl 2,4-dinitrophenyl sulphone	20%
Arylan C.A. (calcium dodecylbenzene sulphonate)	5%
Ethylan B.V. (an octylphenyl-polyethylene oxide condensate)	5%
Toluene	to 100%
(b) 2,4-Dinitrophenyl phenyl sulphoxide	4%
Insem 108 (an oleic acid ester of a glycol)	10%
Benzene	to 100%
(c) Isobutyl 2,4-dinitrophenyl sulphone	16%
Arylan C.A.	2.5%
Ethylan B.V.	2.5%
Isophorone/Xylene blend (30 : 70)	to 100%.

In so far as solubility in suitable solvents allowed, similar compositions were made using other active ingredients hereinbefore listed.

## EXAMPLE 5.

In the preparation of a composition suitable for generation as an aerosol by mechanical means, the following were mixed:

Isobutyl 2,4-dinitrophenyl sulphone	20%
A mixture of acetone (95)% and arachis oil (5%)	to 100%.

## EXAMPLE 6.

- 20 To a mixture of *p*-chlorophenyl 2,4-dinitrophenyl sulphide (31 gms.) and glacial acetic acid (300 mls) at 100° C., there was added 30% hydrogen peroxide (17.5 mls). The resulting mixture was heated on the steam bath  
25 for 18 hours and then water (30 mls) was added and the solution cooled. The crystal-

line material so obtained was recrystallised from benzene to give *p*-chlorophenyl 2,4-dinitrophenyl sulphoxide in the form of a crystalline solid, m.p. 144.5—145.5° C. (Found: C, 44.5; H, 2.3; N, 8.9.  $C_{12}H_7ClN_2O_5S$  requires C, 44.1; H, 2.1; N, 8.6%).

In a similar manner the following compounds were prepared:

*p*-Bromophenyl 2,4-dinitrophenyl sulphoxide, m.p. 138—140°C.  
(Found: C, 39.0; H, 2.1  $C_{12}H_7BrN_2O_5S$  requires C, 38.8; H, 1.9%).

*p*-Fluorophenyl 2,4-dinitrophenyl sulphoxide, m.p. 117—118°C.  
(Found: C, 46.1; H, 2.5  $C_{12}H_7FN_2O_5S$  requires C, 46.5; H, 2.3%).

*p*-Tolyl 2,4-dinitrophenyl sulphoxide, m.p. 131—134°C.  
(Found: C, 51.1; H, 3.7.  $C_{13}H_{10}N_2O_5S$  requires C, 51.0; H, 3.3%).

2,5-Dichlorophenyl 2,4-dinitrophenyl sulphoxide, m.p. 216—220°C.  
(Found: 39.4; H, 1.7.  $C_{12}H_6Cl_2N_2O_5S$  requires C, 39.8; H, 1.7%).

*p*-Chlorobenzyl 2,4-dinitrophenyl sulphoxide, m.p. 152—153°C.  
(Found: C, 45.5; H, 2.9.  $C_{13}H_9ClN_2O_5S$  requires C, 45.8; H, 2.6%).

*p*-Nitrobenzyl 2,4-dinitrophenyl sulphoxide, m.p. 184—186°C.  
(Found: C, 44.7; H, 2.6.  $C_{12}H_9N_3O_5S$  requires C, 44.4; H, 2.6%).

2-Chloro-4-methylphenyl 2,4-dinitrophenyl sulphoxide, m.p. 145—148°C.  
(Found: N, 8.2.  $C_{13}H_9ClN_2O_5S$  requires N, 8.2%).

2-Chloro-5-methylphenyl 2,4-dinitrophenyl sulphoxide, m.p. 210—212°C.  
(Found: N, 8.2.  $C_{13}H_9ClN_2O_5S$  requires N, 8.2%).

*n*-Hexyl 2,4-dinitrophenyl sulphoxide, m.p. 63—65°C.  
(Found: C, 47.9; H, 5.5.  $C_{12}H_{16}N_2O_5S$  requires C, 48.0; H, 5.3%).

*n*-Heptyl 2,4-dinitrophenyl sulphoxide, m.p. 74—76°C.  
(Found: C, 50.0; H, 5.7.  $C_{13}H_{18}N_2O_5S$  requires C, 49.7; H, 5.7%).

#### EXAMPLE 7.

- 5 *p*-Nitrophenyl 2,4-dinitrophenyl sulphide (5 gms) was slowly added to fuming nitric acid (35 mls), the temperature being maintained below 40°C. After standing at room temperature for 6 hours the mixture was poured into water, and the precipitate collected and re-
- crystallised from ethyl acetate and from benzene to give *p*-nitrophenyl 2,4-dinitrophenyl sulphoxide, m.p. 163—164°C. (Found: C, 51.5; H, 3.2; N, 10.6.  $C_{12}H_9N_3O_5S$  requires C, 52.0; H, 3.1; N, 10.1%).
- 15 In a similar manner the following compounds were prepared:

*n*-Pentyl 2,4-dinitrophenyl sulphoxide, m.p. 66—69°C.  
(Found: C, 46.3; H, 5.0.  $C_{11}H_{14}N_2O_5S$  requires C, 46.2; H, 4.9%).

3-Methylbutyl 2,4-dinitrophenyl sulphoxide, m.p. 67—67.5°C.  
(Found: C, 46.2; H, 4.9.  $C_{11}H_{14}N_2O_5S$  requires C, 46.2; H, 4.9%).

Cyclopentyl 2,4-dinitrophenyl sulphoxide, m.p. 119°C. (dec.)  
(Found: C, 46.5; H, 4.3.  $C_{11}H_{12}N_2O_5S$  requires C, 46.5; H, 4.3%).

Cyclohexyl 2,4-dinitrophenyl sulphoxide, m.p. 140°C. (dec.)  
(Found: N, 9.8.  $C_{12}H_{14}N_2O_5S$  requires N, 9.4%).

#### EXAMPLE 8.

- 20 To a solution of *p*-bromophenyl 2,4-dinitrophenyl sulphoxide (9 gms) in concentrated sulphuric acid (25 mls), there was added concentrated nitric acid (25 mls), keeping the temperature below 20°C. After stirring for 1½ hours at room temperature, the mixture was heated on the steam bath for 45 minutes and
- precipitate was collected and recrystallised from glacial acetic acid and from benzene to give 4-bromo-3-nitrophenyl 2,4-dinitrophenyl sulphoxide, m.p. 180—182°C. (Found: C, 34.2; H, 1.6.  $C_{12}H_6BrN_3O_5S$  requires C, 34.6; H, 1.4%).
- 25 then cooled and poured into iced water. The
- 30 In a similar manner the following compounds were prepared:

4-Chloro-3-nitrophenyl 2,4-dinitrophenyl sulphoxide, m.p. 182—185°C.  
(Found: C, 38.8; H, 1.9.  $C_{12}H_6ClN_3O_5S$  requires C, 38.8; H, 1.6%).

3-Nitrophenyl 2,4-dinitrophenyl sulphoxide, m.p. 210—212°C.  
(Found: C, 43.0; H, 1.8.  $C_{12}H_7N_3O_5S$  requires C, 42.7; H, 2.1%).

#### EXAMPLE 9.

- 35 2,4-Dinitrophenyl 4-methoxyphenyl sulphide (2 gms) in ether (200 mls) was treated with monoperphthalic acid (25.2 mls) and left for several days at 0°C. The solution was evapor-
- ated to dryness, the residue washed with water and sodium bicarbonate solution and recrystallised from benzene to give 2,4-dinitrophenyl 4-methoxyphenyl sulphoxide m.p. 150—152°C. (Found: N, 8.9.  $C_{11}H_{11}N_2O_5S$  requires N, 8.7%).
- 40
- 45



## EXAMPLE 10.

2,5 - Dichlorophenyl 2,4 - dinitrophenyl sulphoxide (14 gms) was slowly added to fuming nitric acid (70 mls), and the reaction mixture was poured into water. The precipitate was collected and dissolved in glacial acetic acid (1200 mls) and after allowing this solution to stand for 5 days, a solid precipitate was obtained and isolated. Recrystallisation from tetrachloroethane gave 2,5-dichloro-x-nitrophenyl 2,4-dinitrophenyl sulphoxide, m.p. 238—242° C., which set to give large prisms, m.p. 251° C. (Found: C, 35.4; H, 1.5.  $C_{12}H_2Cl_2N_2O_5S$  requires C, 35.5; H, 1.2%).

## EXAMPLE 11.

To 25 mls of fuming nitric acid there was added 4-carboxyphenyl 2,4-dinitrophenyl sulphide (5 gms) and after standing at room temperature for 16 hours the reaction mixture was poured into water. The precipitate so obtained was recrystallised from acetic acid, giving a first crop of 4-carboxyphenyl 2,4-dinitrophenyl sulphoxide, m.p. 237—239° C. From the mother liquor, a further crop of material was obtained and this was heated under reflux with methanol (100 mls) and sulphuric acid (1 ml) for 3 hours. A clear solution was obtained which on cooling produced yellow crystals which were found to possess a double melting point. The crystals were boiled with a small quantity of methanol and the insoluble material separated. Cooling of the methanol gave a solid product which was collected and recrystallised from methanol to give *p*-methoxycarbonylphenyl 2,4-dinitrophenyl sulphoxide, m.p. 133—135° C. (Found: C, 48.0; H, 2.9.  $C_{11}H_9N_2O_5S$  requires C, 48.0; H, 2.9%).

The material insoluble in hot methanol was recrystallised from acetic acid to give 4-methoxycarbonyl-x-nitrophenyl 2,4-dinitrophenyl sulphoxide, m.p. 240—242° C. (Found: C, 42.9; H, 2.5; N, 10.7.  $C_{11}H_8N_2O_5S$  requires C, 42.5; H, 2.3; N, 10.6%).

## EXAMPLE 12.

*p*-Chlorobenzyl 2,4-dinitrophenyl sulphide (5 gm), glacial acetic acid (200 ml) and 30% hydrogen peroxide (7 ml) were heated at 95° C for 30 hours. After standing overnight at room temperature, the reaction mixture was diluted with water and the precipitate collected and recrystallised from Cellosolve—(Registered Trade Mark). Two different crystals were obtained, needles m.p. 154—156° C. and prisms, m.p. 177—182° C. These were separated roughly by hand and the prisms recrystallised from acetic acid to give *p*-chlorobenzyl, 2,4-dinitrophenyl sulphone, m.p. 184—185° C. (Found: C, 43.9; H, 2.8.  $C_{10}H_7ClN_2O_5S$  requires C, 43.8; H, 2.8%).

In a similar manner the following compounds were prepared by oxidation of the appropriate sulphides. *p*-Nitrobenzyl 2,4-di-

nitrophenyl sulphone, m.p. 229—232° C. (Found: C, 42.7; H, 2.5.  $C_{11}H_8N_2O_5S$  requires C, 42.5; H, 2.5%).

3-Chloropropyl 2,4-dinitrophenyl sulphone, m.p. 80—81° C. (Found: Cl, 12.0.  $C_{10}H_7ClN_2O_5S$  requires Cl, 11.5%).

## EXAMPLE 13.

2,4-Dinitrophenylsulphonylacetic acid in acetic acid was treated with bromine (10% excess) and the mixture heated under reflux for  $\frac{1}{2}$  hour while hydrogenbromine was evolved. The product was recrystallised from acetic acid to give dibromomethyl 2,4-dinitrophenyl sulphone, m.p. 158—160° C. (Found: C, 20.7; H, 1.2.  $C_7H_4Br_2N_2O_5S$  requires C, 20.8; H, 1.0%).

Similarly, using chlorine in place of bromine, there was obtained dichloromethyl 2,4-dinitrophenyl sulphone, m.p. 150—152° C. (Found: C, 27.0; H, 1.4.  $C_7H_4Cl_2N_2O_5S$  requires C, 26.7; H, 1.3%).

2,4-Dinitrophenylsulphonylacetic acid employed as starting material in the above preparations was prepared from methyl 2,4-dinitrophenylthioacetate, which was oxidised with hydrogen peroxide to give methyl 2,4-dinitrophenylsulphonylacetate, and this latter ester was then hydrolysed.

## EXAMPLE 14.

To a mixture of 2,4-dinitrophenyl *p*-tolyl sulphide (29 gm.), glacial acetic acid (100 ml.) and concentrated sulphuric acid (1 ml.), at 52° C., there was added 30% hydrogen peroxide (12.3 ml.). During addition the reaction mixture was maintained below 55° C. by external cooling and after maintaining at 50° C. for a further hour, it was poured into a large excess of water. The precipitate was dried to give 2,4-dinitrophenyl *p*-tolyl sulphoxide, m.p. 134.5—136.5° C. (Found: C, 51.0; H, 3.3.  $C_{12}H_{10}N_2O_5S$  requires C, 51.0; H, 3.3%).

## WHAT WE CLAIM IS:—

1. A fungicidal composition comprising as an active ingredient a compound of the general formula:



in which *n* represents 1 or 2 and (a) when *n* = 1, R represents a radical selected from alkyl containing 5—7 carbon atoms, cycloalkyl, phenylalkyl, phenylalkyl in which the phenyl nucleus contains one or more substituents selected from halogen atoms and nitro groups, phenyl and phenyl which contains one or more substituents selected from halogen atoms, nitro, alkyl, alkoxy and alkoxy carbonyl groups, (b) when *n* = 2, R represents a radical selected

from alkyl, halogenated methyl, halogenated propyl, cycloalkyl, phenylalkyl and phenylalkyl in which the phenyl nucleus contains one or more substituents selected from halogen atoms and nitro groups; in association with an inert fungicidal adjuvant.

2. A composition as claimed in claim 1 comprising a compound from the following list:

- 10 n-butyl 2,4-dinitrophenyl sulphone.
- isobutyl 2,4-dinitrophenyl sulphone.
- n-pentyl 2,4-dinitrophenyl sulphone.
- p-tolyl 2,4-dinitrophenyl sulphoxide.
- 15 p-methoxycarbonylphenyl 2,4-dinitrophenyl sulphoxide.

3. A composition as claimed in claim 1 or 2 and in a form suitable for dilution with water to produce an aqueous spraying liquid, in which the inert fungicidal adjuvant comprises one or more diluents selected from dispersing agents, emulsifying agents and wetting agents.

4. A composition as claimed in claim 1 or 2 and in the form of a dusting powder, in which the inert fungicidal adjuvant comprises a pulverulent solid diluent.

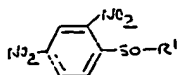
5. A composition as claimed in claim 1 or 2 and suitable for dispersion as an aerosol in which the inert fungicidal adjuvant comprises one or more diluents selected from volatile solvents, non-volatile oils, high boiling aromatic solvents and volatile propellants.

6. A composition as claimed in claim 1 or 2 and suitable for the generation of a smoke containing the active ingredient, in which the inert fungicidal adjuvant comprises an ignitable slow-burning composition.

7. Compositions as claimed in any of claims 1—6 substantially as herein described.

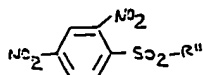
8. Compositions as claimed in claim 1 or 2 substantially as described in Examples 1—5.

9. Compounds of the general formula:



45 wherein R<sup>1</sup> represents an alkyl radical containing 5—7 carbon atoms, a halogenated and/or nitrated benzyl radical, a cycloalkyl radical, or a substituted phenyl radical in which the substituents are selected from halogen atoms, nitro, alkyl, alkoxy and alkoxy carbonyl radicals, provided that R<sup>1</sup> does not represent 2,4-dinitrophenyl or o-methoxycarbonylphenyl.

10. Compounds of the general formula:



wherein R<sup>11</sup> represents a dichloromethyl, di-

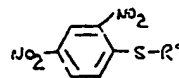
bromomethyl, 3-chloropropyl or a halogenated and/or nitrated benzyl radical.

11. p-Tolyl 2,4-dinitrophenyl sulphoxide.

12. p-Methoxycarbonylphenyl 2,4-dinitrophenyl sulphide.

13. A process for the preparation of compounds claimed in any of claims 9 to 12 which comprises oxidising the corresponding sulphides.

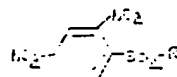
14. A process for the preparation of compounds claimed in any of claims 9 to 12 which comprises oxidising a compound of the general formula:



in which R<sup>2</sup> is a radical readily transformable into the desired radical R<sup>1</sup> or R<sup>11</sup> by subsequent treatment, and treating the sulphoxide or sulphone so obtained by suitable means to produce a radical R<sup>1</sup> or R<sup>11</sup> in place of R<sup>2</sup>.

15. Compounds whenever prepared by the processes claimed in claims 13 or 14.

16. A method of controlling the growth of fungi on a crop which comprises treating the crop or the soil in which the crop is to grow with a fungicidally effective amount of a compound of the general formula:



in which n represents 1 or 2 and (a) when n = 1, R represents a radical selected from alkyl containing 5—7 carbon atoms, cycloalkyl, phenylalkyl, phenylalkyl in which the phenyl nucleus contains one or more substituents selected from halogen atoms and nitro groups, phenyl and phenyl which contains one or more substituents selected from halogen atoms, nitro, alkyl, alkoxy and alkoxy carbonyl groups, (b) when n = 2, R represents a radical selected from alkyl, halogenated methyl, halogenated propyl, cycloalkyl, phenylalkyl and phenylalkyl in which the phenyl nucleus contains one or more substituents selected from halogen atoms and nitro groups.

17. A method according to claim 16 in which said compound is applied at a rate of 0.2—100 lb. per acre.

18. A method according to claim 16 in which said compound is applied at a rate of 0.2—8 lb. per acre.

19. A method according to claim 16 in which said compound is applied to the crop at a rate of 0.5—2 lb. per acre in the form of an aqueous spray.

20. A method according to any of claims 16—19 in which said fungi are selected from

- Venturia* spp., *Phytophthora* spp., genera of the family *Peronosporaceae*, *Cladosporium* spp., *Alternaria* spp., *Septoria* spp., *Botrytis* spp., *Sclerotinia* spp. and *Gloeosporium* spp.
- 5 21. A method according to any of claims 16—20 in which said crop is selected from apples, pears, potatoes, vines, celery, broad beans, tomatoes and stone fruits.
- 10 22. A method according to claim 21 in which *Venturia inaequalis* is controlled on apples.
23. A method according to any of claims 16—22 in which said compound is selected from:
- n-butyl 2,4-dinitrophenyl sulphone 15  
 isobutyl 2,4-dinitrophenyl sulphone  
 n-pentyl 2,4-dinitrophenyl sulphone  
 p-tolyl 2,4-dinitrophenyl sulfoxide  
 p-methoxycarbonylphenyl 2,4-dinitrophenyl  
 sulfoxide. 20
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